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UNIVERSITY OF SOUTH ALABAMA

DEPARTMENT OF
BIOLOGICAL SCIENCES

USA

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June 27, 1990

Dr. Michael Marron
ONR Code 1141 MB
800 N. Quincy Street
Arlington, VA 22217-5000

Dear Dr. Marron,

Enclosed is our annual report.

We appreciate your support in helping us initiate the project on polypeptide corrosion inhibitors. The project is now at a level where it may be sustainable through other funding mechanisms. The data set has been useful to us in making the case for use of polyamino acids by water treatment companies.

We have enjoyed working with you and look forward to the possibility of pursuing other projects as a part of ONR programs.

Sincerely,

Steve Sikes

C. Steven Sikes
Professor
Department of Biological Sciences
Director
The Mineralization Center

ANNUAL PROGRESS REPORT

GRANT#: N00014-88-K-0428 R&T CODE: 4412050

PRINCIPAL INVESTIGATOR: C. Steven Sikes

INSTITUTE: University of South Alabama, Mineralization Center

GRANT TITLE: Polypeptide Inhibitors of Mineral Scaling and Corrosion

PERIOD OF PERFORMANCE: 1 July, 1989 - 30 June, 1990

OBJECTIVE: To develop and evaluate polypeptide analogs of biomineral matrices as inhibitors of steel corrosion and mineral scale formation in sea water.

ACCOMPLISHMENTS (last 12 months): Novel polyanionic peptides have been synthesized by thermal polymerization, the method itself having new aspects. Both the peptide and the method of synthesis are subjects of patent applications.

Corrosion inhibition has been demonstrated using polyaspartate, the simplest polyanionic peptide, in studies with mild and Type 304 stainless steels exposed to synthetic sea water. In the preliminary studies with mild steel, it was observed that polyaspartate caused an upward shift in the open circuit potential (E_{corr}), suggesting some anodic control of corrosion. However, Tafel analyses of mild steel do not show preferential alteration of the anodic reaction, thus, a mixed control mechanism is suggested.

Replicate Tafel analyses have been conducted with 304 stainless steel under control conditions to determine Tafel slopes and establish basal corrosion rates. Tafel studies in the presence of polypeptides are in progress. Examination of thermal polyaspartate effects on polarization resistance corrosion of 304 stainless steel has begun (Table 1). A typical dose-response curve is obtained when the data are plotted on a log scale. A maximum corrosion inhibition of approximately 30% is obtained with 10 ug/ml of thermal polyaspartate. Greater inhibition may be obtained with peptides modified in primary structure and functional side groups.

Based on studies of polyanionic peptides as crystallization inhibitors, it was predicted that polyanionic peptides would bind metal surfaces, blocking corrosion sites and reactions. Experiments have begun to examine the polypeptide/metal interactions. Figure 1a. shows the surface of a stainless steel control electrode, exposed to sea water to which additional calcium and bicarbonate had been added for 91.5 hours. The EDAX spectrum shows a strong calcium peak. Figure 1b. shows an electrode treated similarly except for a 30 minute pretreatment in normal sea water containing 10 ug ml^{-1} of thermal polyaspartate. EDAX analysis shows no calcium on the surface. The corrosion rate of this electrode was about 1/3 of the control (.0035 vs .0123 mpy). Thus, it appears that the polypeptide was bound to the metal during pre-treatment and was sufficient to prevent calcium carbonate precipitation and inhibit corrosion under supersaturated conditions.

Prior studies of the relationship between $CaCO_3$ deposition and steel corrosion have been conflicting, with both inhibition and promotion of

corrosion reported under mineral layers. Our experiments indicate that both effects are possible and are dependent on the distribution and uniformity of the mineral deposit.

The set-up of a Petrolite corrosion monitor (on loan from NOARL) has been somewhat frustrating with noisy data often unusable. Although some good inhibition measurements have been obtained with 304 stainless steel, we have been unable to demonstrate inhibition of 1018 mild steel with this instrument (although inhibition has been observed with more refined instruments).

SIGNIFICANCE: Synthetic peptides and processes have been developed in this laboratory that may make use of the peptides economically feasible. The value of such peptides will be greatly enhanced if they possess significant corrosion inhibiting activity. The non-toxic and biodegradable nature of polyanionic peptides would make their use particularly attractive to industry as environmentally compatible materials.

WORK PLAN (next 12 months): Much of the progress has been made since Dec., 1989 when Dr. Erich Mueller arrived at our facility and devoted his efforts to this project. The project is now progressing satisfactorily and will concentrate on the following objectives: 1) evaluation of "advanced" polypeptides as corrosion inhibitors, 2) examination of peptide-mineral-metal surface interactions and 3) microbiologically-influenced corrosion and the effects of polypeptides on this phenomenon.

INVENTIONS (last 12 months): Applications for patenting certain polyanionic peptides, their method of thermal synthesis and their use as corrosion inhibitors in water treatment programs are in preparation.

PUBLICATIONS AND REPORTS (last 12 months):

1. A paper and a book originating from an American Chemical Society symposium is in press.

Little, B.J. and C.S.Sikes, in press. Corrosion inhibition by thermal polyaspartate. In: C.S.Sikes and A.P. Wheeler (eds.), Surface Reactive Peptides and Polymers: Discovery and Commercialization. ACS Books: Washington, D.C.

2. A paper is being prepared for submission to the National Association of Corrosion Engineers.

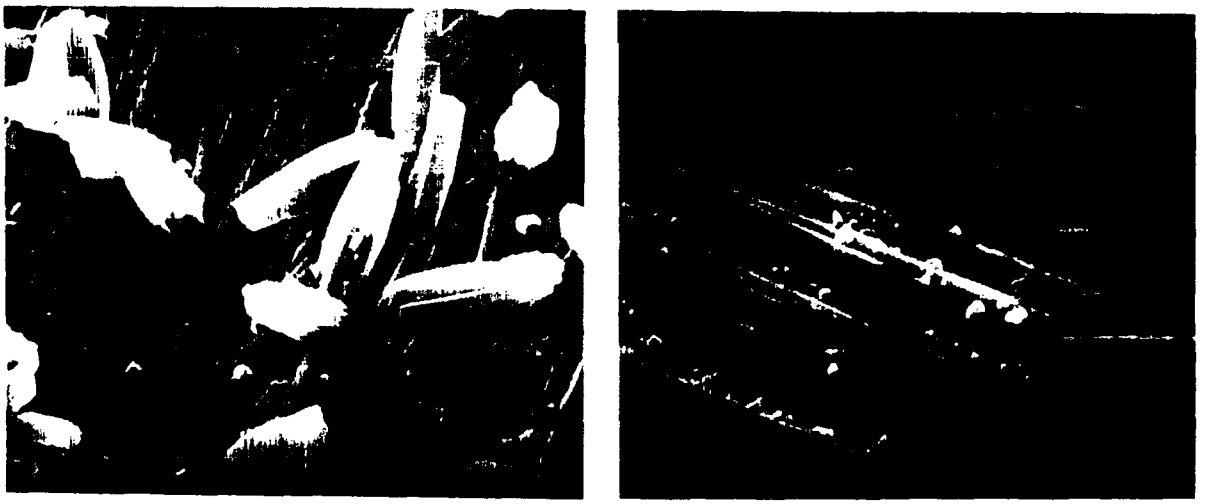
Mueller, Erich and C. Steven Sikes, in prep. Polypeptide inhibitors of steel corrosion in sea water. Corrosion 91.

3. A second paper is also in preparation.

Mueller, E., X. Jiang, P. Wagner, B. Little and C.S. Sikes, in prep. Interactions of polyanionic peptides with steel surfaces and effects on calcium carbonate deposition.

polyaspartate concentration (ug ml^{-1})	% inhibition of control corrosion rate		
	mean	SD	N
.1	6.31	.37	2
.5	7.95	4.74	2
1.0	17.70	5.95	4
5.0	28.27	6.60	4
10.0	30.51	4.14	4
20.0	29.90	2.55	2
50.0	30.20	N/A	1

Table 1. Inhibition of 304 stainless steel corrosion by thermal polyaspartate. Corrosion was determined by polarization resistance using a Petrolite 6000 corrosion monitor.



a. b.

Figure 1. Scanning electron micrographs of Type 304 stainless steel electrode surfaces. Electrodes were exposed to artificial sea water supersaturated with calcium carbonate for 91.5 hours. Both images taken at 30 kV, 2000 X magnification. a. 30 minute pretreatment in sea water only. b. 30 minute pretreatment in sea water containing 10 ug ml^{-1} polyaspartate. Images, and EDAX analysis (not shown), performed by Ms. Pat Wagner at the Naval Oceanographic and Atmospheric Research Laboratory, Stennis Space Center, MS.

Objectives

- Develop peptide analogs of biomineral matrices
- Measure inhibition of steel corrosion by peptides
- Determine if peptides inhibit scale formation on steel surfaces

Accomplishments

- Developed new peptides and methods of thermal synthesis
- Determined dose-response relationship for a peptide on SS corrosion
- Inhibited crystallization on SS surface pretreated with peptide

Significance

- Peptides may be effective in water treatment for:
  - corrosion control
  - scale control
- Peptides environmentally compatible

C.S. Sikes, A.P. Wheeler and B.J. Little

University of South Alabama
Mineralization Center

1990

Principal Investigator: C.S. Sikes

Institute: Mineralization Center
LSB 124
University of South Alabama
Mobile, AL 36608

Grant title: Polypeptide Inhibitors of Mineral Scaling and Corrosion

Period of performance: 1 July, 1989 to 30 June, 1990

Number of publications last year: 2

Number of patents/inventions: 1

Total number of students/trainees: 2

How many are female? 1

How many are minority students (e.g. Black, Hispanic)? 1

How many are not US citizens? 1

Awards/Honors to PI and/or to members of PI's research group (please describe):

Dr. Sikes was named The Dean's Lecturer by The College of Arts and Sciences. This is an annual award for scholarship.

Equipment purchased (# and description of items >$1500):

A galvanostat/potentiostat from Princeton Applied Research was purchased using matching funds from the State of Alabama. No equipment was purchased using ONR funds.

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FØ1T@USOUTHAL (bitnet)

Our Email address on Internet is: marron@ccf3.nrl.navy.mil
This address can be reached via Arpanet or Bitnet. We read our mail daily.